# END FUNCTIONALIZATION OF CARBON NANOTUBES

## Background

This invention relates generally to the formation and utilization of carbon nanotube structures.

Carbon nanotubes are graphene cylinders whose ends are closed by caps including pentagonal rings. The nanotube is a hexagonal network of carbon atoms forming a seamless cylinder. These cylinders can be as little as a nanometer in diameter with lengths of tens of microns in some cases. Depending on how they are made, the tubes can be multiple walled or single walled.

The carbon nanotubes may become the building blocks for mechanical, electronic, and biological structures. However, such applications require combining carbon nanotubes with one or more other elements. One way to combine these carbon nanotubes is to functionalize the nanotubes and then combine them with other chemicals or molecules.

Thus, there is a need for better ways of functionalizing carbon nanotubes.

## Brief Description of the Drawings

Figure 1 is a perspective view of one embodiment of the present invention at an early stage of manufacture;

Figure 2 is a perspective view of the embodiment shown in Figure 1 after further processing in accordance with one embodiment of the present invention;

Figure 3 is a perspective view of the embodiment shown in Figure 2 after further processing in accordance with one embodiment of the present invention;

Figure 4 is a perspective view of the embodiment shown in Figure 3 after further processing in accordance with one embodiment of the present invention;

Figure 5 is a perspective view of the embodiment shown in Figure 4 after further processing in accordance with one embodiment of the present invention;

Figure 6 is a vertical, cross-sectional view for an embodiment generally similar to Figure 1 or Figure 5 in accordance with one embodiment of the present invention;

Figure 7 is a cross-sectional view of the embodiment shown in Figure 6 after further processing in accordance with one embodiment of the present invention;

Figure 8 is a cross-sectional view corresponding to Figure 7 after further processing in accordance with one embodiment of the present invention;

Figure 9 is a cross-sectional view corresponding to Figure 8 after further processing in accordance with one embodiment of the present invention;

Figure 10 is a cross-sectional view of the embodiment shown in Figure 9 after further processing in accordance with one embodiment of the present invention;

Figure 11 is a cross-sectional view corresponding to Figure 10 after further processing in accordance with one embodiment of the present invention;

Figure 12 is a cross-sectional view further corresponding to Figure 6 in accordance with another embodiment of the present invention;

Figure 13 is a cross-sectional view corresponding to Figure 12 after further processing in accordance with one embodiment of the present invention;

Figure 14 is a cross-sectional view corresponding to Figure 13 after further processing in accordance with one embodiment of the present invention;

Figure 15 is a cross-sectional view corresponding to Figure 14 after further processing in accordance with one embodiment of the present invention;

Figure 16 is a cross-sectional view corresponding to Figure 15 after further processing in accordance with one embodiment of the present invention;

Figure 17 is a cross-sectional view corresponding to Figure 16 after further processing in accordance with one embodiment of the present invention;

Figure 18 is a cross-sectional view corresponding to Figure 6 in accordance with another embodiment of the present invention;

Figure 19 is a cross-sectional view of the embodiment shown in Figure 18 after further processing in accordance with one embodiment of the present invention;

Figure 20 is a cross-sectional view corresponding to Figure 19 after further processing in accordance with one embodiment of the present invention;

Figure 21 is a cross-sectional view corresponding to Figure 20 after further processing in accordance with one embodiment of the present invention;

Figure 22 is a cross-sectional view of the embodiment shown in Figure 21 after further processing in accordance with one embodiment of the present invention;

Figure 23 is a cross-sectional view corresponding to Figure 22 after further processing in accordance with one embodiment of the present invention;

Figure 24 is a cross-sectional view corresponding to Figure 23 after further processing in accordance with one embodiment of the present invention;

Figure 25 is a cross-sectional view corresponding to Figure 24 after further processing in accordance with one embodiment of the present invention;

Figure 26 is a cross-sectional view of another embodiment of the present invention;

Figure 27 is a top plan view of another embodiment of the present invention; and

Figure 28 is a side elevational view of the embodiment shown in Figure 27 after further processing in accordance with one embodiment of the present invention.

## Detailed Description

Referring to Figure 1, carbon nanotubes 10 may be aligned on a substrate 12. The alignment may be accomplished using electric fields or molecular combining as two examples.

The substrate 12 and carbon nanotubes 10 are then covered with a photoresist layer 14 as shown in Figure 2. The photoresist layer 14 is patterned by lithography as shown in Figure 3 to form a mask 14a over the carbon nanotubes 10. Plasma etching, indicated as $O_2$ etching in Figure 4, may be applied to cut nanotubes 10 into uniform length as shown in Figure 5. The lithography may include photolithography, e-beam lithography, or other lithography. While an oxygen plasma etching process is illustrated, other techniques are possible as well.

As shown in Figure 6, a carbon nanotube 10 may be aligned on a substrate 12. A number of other carbon nanotubes 10 aligned generally parallel to the illustrated nanotube 10 may be arranged extending into the page in Figure 6.

Thereafter, the nanotubes 10 and the substrate 12 may be coated with photoresist 16 as shown in Figure 7. Lithography may be utilized to expose the end portions of the carbon nanotubes as shown in Figure 8. Oxygen plasma etching (Figure 9) may then burn out the exposed end portions of the carbon nanotubes 10. The carbon nanotubes 10 are then cut to the length defined by the lithography.

The cut nanotubes 10 have open ends. A solution of chemical agents (layer 18) is then applied to the ends of nanotubes. The sidewalls of the nanotubes are still protected by photoresist 16. As a result, chemicals in the layer 18 (Figure 10) can only access the open ends of the carbon nanotubes 10. One or more functional groups from the layer 18 may be attached to the open ends of the carbon nanotubes 10 from the chemical laden layer 18. Without limiting the scope of the present invention, the layer 18 may include carboxylic or amine groups. The layer 18 containing different chemicals can be applied more than once to attach multiple functional groups to the ends of nanotubes.

As shown in Figure 11, the photoresist 16 and the chemical laden layer 18 may be removed to obtain the functionalized carbon nanotube 10. The ends A and B may both be functionalized in one embodiment.

Referring to Figures 12 through 17, a single end functionalization technique is illustrated. The end to be

functionalized is illustrated as B in Figure 12. The carbon nanotube 10 may be covered with photoresist 16 as shown in Figure 13. Lithography is utilized to expose only end B of the carbon nanotube 10, as indicated in Figure 14. The carbon nanotube 10 may be cut off to length using oxygen plasma etching as shown in Figure 15. The exposed, open-ended tube 10 may then be coated with a chemical laden layer 18 to end functionalize the end B of the carbon nanotube 10, as shown in Figure 16. In Figure 17, the chemical laden layer 18 and the photoresist 16 may be removed. At this point, only the end B of the carbon nanotube 10 is functionalized. Applying the same process to end A may functionalize end A with a different molecule. The tube length may be defined by the lithography in the two-step end functionalization process.

Referring to Figures 18 through 25, the end A is to be functionalized with a chemical that may not be compatible with photoresist. The carbon nanotube 10 may be covered by a layer of photoresist 16 as indicated in Figure 19. The end B of the carbon nanotube 10 may then be exposed (Figure 20) using conventional photolithography process to remove a portion of the photoresist 16. Thereafter, a layer of silicon dioxide or another protection material 20 may be deposited over the structure as shown in Figure 21. The deposition may be done using conventional chemical vapor deposition and lithography in one embodiment.

Thereafter, the underlying photoresist 16 may be removed, resulting in the structure shown in Figure 22. The exposed portion of the carbon nanotube 10 (not covered by the silicon dioxide 20) may then be removed using oxygen plasma etching as shown in Figure 23. The resulting structure may then be covered with an end functionalizing chemical 18 to end functionalize the open ended carbon nanotube 10 in Figure 24. Thereafter, the chemical 18 and the silicon dioxide 20 may be removed as shown in Figure 25.

Referring next to Figure 26, the end functionalized carbon nanotubes 10 may be utilized for self-assembly of carbon nanotube arrays. The functionalized ends A and B are arranged so that the end B extends vertically and the end A is attached to a structure 24 to which it is attracted. The structure 24 is also functionalized with molecules that specifically bind to the functional groups on the ends A of the carbon nanotubes 10 and not the functional groups on the ends B. The end functionalized carbon nanotubes 10 already have one end A attached to the structure 24. The other end B may stay in solution. The resulting structure may form a self-aligned vertical array with uniform thickness. An example of one application is for thermal interface material (TIM) fabrication.

Referring to Figure 27, end functionalized carbon nanotubes 10 may be utilized for self-assembly of an

organized carbon nanotube array at a specific location and orientation on the substrate 26. An area 30 of the substrate 26 is functionalized with molecules that specifically bind with functional group on the end A. Another area 28 is functionalized with molecules that specifically bind with functional group B on the opposite end B of the carbon nanotubes 10. If the distance between the attachment points is equal to the length of the end functionalized carbon nanotubes 10, the first end A of the functionalized carbon nanotubes 10 binds to the area 30 and the second end B binds to the area 28.

Referring to Figure 28, the structure shown in Figure 27 may be further processed to include a gate dielectric layer 32 and a gate electrode 34. The use of an array of nanotubes 10 may increase the current drive of a transistor formed using the nanotubes 10 as an effective channel. The transistor may include a source 30 and a drain 28 that are functionalized to attach to specific carbon nanotube functionalized ends A and B.

In one embodiment, a deoxyribonucleic acid (DNA) molecule may include the information to drive the self-assembly process. A single stranded DNA molecule may be attached to the end of a carbon nanotube using the method described above. The single stranded DNA may have a sequence complementary to another single stranded DNA molecule or to a linker of a double stranded DNA at desired

locations. The two DNA molecules may be bound to each other according to sequence matching between the two types of DNA molecules, and thus immobilize the end of the nanotube to the desired location.

The carbon nanotubes 10 may be functionalized with a protein streptavidin. That protein may bind to an antibody that attaches to a specific location, locating the nanotube 10 at the correct address. The nanotube assembly may be placed on a passivated, oxidized silicon wafer before metallization.

In some embodiments of the present invention it is possible to select to functionalize only one or more ends of a carbon nanotube. In some embodiments different ends may be functionalized with different molecules. Lithography and etching methods may be utilized to selectively expose one end of a carbon nanotube. The exposed end can then be chemically functionalized and may be connected with one or more other functional groups of available molecules. The second end of the carbon nanotube can be exposed by repeating the lithography and etching process. The second end of the carbon nanotube may then be functionalized with a second functional group or be connected with one or more available molecules.

In addition, end functionalized carbon nanotubes of uniform length may be utilized for these procedures. The different functionalizations at the two ends of the

nanotubes may be useful in self-assembly and pattern formation for building components of carbon nanotubes. For example, it may be useful for biosensors.

Carbon nanotubes may be made either polar or amphiphilic by appropriate modification. One end of the resulting carbon molecule may then be immobilized and alignment may be achieved through molecular combing. One end only may be functionalized with biomolecules and the structure may then be utilized for a biosensor in one embodiment.

While the present invention has been described with respect to a limited number of embodiments, those skilled in the art will appreciate numerous modifications and variations therefrom. It is intended that the appended claims cover all such modifications and variations as fall within the true spirit and scope of this present invention.

What is claimed is: